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**Lightening dyed textile material**

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5 This invention relates to a process for lightening or partially decolorizing vat- or sulfur-dyed textile materials, which comprises treating the material with aminoalkanesulfinic acids in a neutral or weakly acidic medium, and to preparations of the aminoalkanesulfinic acids for carrying out this process.

10 In vat and sulfur dyeing, textile materials comprising cellulosic fibers, such as cotton, linen, hemp or regenerated cellulose fibers such as modal fibers or unmodified viscose rayon, with or without other, especially synthetic, fibers, eg. polyester fibers, for  
15 example cotton textiles or cotton-polyester blend textiles, are treated with vatted vat or sulfur dyes in an alkaline medium. After the vatted dye has gone onto the cellulosic fiber, the textile material is rinsed neutral and then reoxidized.

20 Vatting is the conversion of certain water-insoluble dyes (vat dyes or sulfur dyes) by reduction in an alkaline medium into a water-soluble hydro or leuco compound whose anion has sufficient affinity for fiber composed of natural or regenerated cellulose, for  
25 example cotton fiber or rayon. On reoxidation of the leuco compound, for example by exposure to air, the insoluble dye is re-formed in a very finely divided stage in the cellulosic fiber and thus ensures high-grade wash- and crock- and lightfastness.

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Vat and sulfur dyes may be applied to textiles at every stage of processing, ie. not only to fabrics, such as

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Hardwearing workwear items and, these days, blue jeans especially are generally manufactured using a coarse cotton fabric (denim), which is customarily dyed with the vat dye indigo. To create the typical appearance of a pair of blue jeans, generally only the warp threads are dyed prior to weaving and the weft is left colorless. After weaving and making up, it is frequently desired that the garment be partially decolorized again. In fact, only exposed areas of the garment are to be decolorized, the seams for example. Moreover, the pronounced color contrast between the dyed warp threads and the colorless weft threads is to be preserved, ie. the latter must not become stained in the course of the lightening process. There is frequently also a desire to achieve a particular visual effect, for example the "used look" or that only

exposed, comparatively highly stressed areas are lightened.

5 The partial subsequent removal of dye can be effected  
for example mechanically by washing in the presence of  
pumice, enzymatically by the partial destruction of the  
cellulose, or chemically by altering or destroying the  
dye (stripping). A frequent choice is the stonewashing  
10 method, where the fabric is treated mechanically with  
pumice and/or cellulases. Stonewashing is time-  
consuming and inconvenient, since the pumice stones  
have to be removed again from the material, and this is  
at least partly done by hand. The stones are  
responsible for abrading the equipment and major  
15 amounts of sludge arise and have to be disposed of. The  
visual effect obtained in this way is very good, but  
the lightening effect is only minimal, so that  
generally a bleaching process is carried out in  
addition.

20 The bleach can be effected enzymatically, oxidatively  
or reductively.

25 An ecologically particularly advantageous bleach is the  
enzymatic bleach by means of laccases which is  
described in WO 97 25 469. However, laccases are so  
costly that this process is too uneconomical for  
everyday textile finishing practice.

30 The oxidative removal of dyes may be carried out for  
example using strong oxidizing agents such as alkali  
metal hypochlorite, ozone or alkali metal permanganate.  
However, oxidative processes are disadvantageous  
because of the pronounced fiber damage and, especially  
35 in the case of the use of hypochlorites, the  
unfavorable ecological aspects (AOX).

Despite these disadvantages, oxidative dye destruction today is customarily carried out using hypochlorite.

5 Reductive removal of vat and sulfur dyes may be effected using various reducing agents, albeit subject to specific restrictions if only partial removal of the dye is desired.

10 Very strong reducing agents (for example alkali metal dithionite or thiourea dioxide) are unsuitable, since they provide much too rapid and complete, in some instances instantaneous, vatting of many vat dyes, especially indigo, for example. As a result, much too much dye is stripped off in uncontrolled fashion. Weak  
15 reducing agents, by contrast, such as glucose or hydroxyacetone, require a relatively high processing temperature, a high pH, ie. a relatively large amount of alkali metal (eg. sodium or potassium) hydroxide, and a high concentration of the reducing agent. In  
20 addition, the treatment time is relatively long. Moreover, organic reducing agents, such as glucose, for example, are no longer acceptable in wastewater owing to their high chemical oxygen demand (COD); and the washing until neutral is very costly. Despite these  
25 problems, relatively mildly reductive bleaching agents, for example, glucose, are still being used where necessary (JP 96-270034).

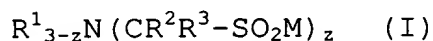
30 The vat dye detached from the warp should not stain the colorless weft threads, which tends to happen under reductive conditions, for example in the presence of alkaline glucose solution. It is therefore customary to include in the wash liquor a backstain inhibitor to control any backstaining by the dissolved dye because  
35 the dissolved dye generally has greater affinity for the backstain inhibitor than for the fiber.

An improved reductive bleaching process, using hydroxyalkanesulfinic acids as bleaching agents, is described in DE-A-19 708 973. The disadvantage of this process is that it too has to be carried out in a strongly alkaline medium with its attendant backstaining and the associated low color contrast.

It is an object of the present invention to provide a process for the controlled decolorizing or lightening of vat- or sulfur-dyed textile materials whereby the aforementioned disadvantages are avoided or reduced and whereby an optimum color contrast (washdown effect) is achieved relatively consistently, rapidly and environmentally safely especially in the partial decolorizing (lightening) of denim fabrics.

We have found that, surprisingly, this object is achieved by the textile finishing process of the invention described hereinbelow.

The present invention accordingly provides a process for controlled preferably partial, decolorization (lightening) of vat- or sulfur-dyed or -printed textile material, especially denim fabric, which comprises treating the textile material to be lightened or decolorized with one or more compounds (aminoalkanesulfinates) of the formula I



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where

z is 1, 2 or 3,

$R^1$  is

a) when z is 1 or 2: hydrogen, alkyl of 1 to 18 carbon atoms or  $HOCH_2CH_2$ ,

35 b) when z is 2: additionally OH, and

c) when  $z$  is 1: either as defined under a) independently for the two  $R^1$  radicals or as defined under a) in one instance and as defined under b) in the other,

5  $R^2$  and  $R^3$ , which may be the same or different, are each hydrogen or alkyl of 1 to 4 carbon atoms subject to the proviso that together they have not more than 4 carbon atoms, and

10 M is one equivalent of a mono- or divalent metal atom, at pH 4 - 7, followed if desired by an aftertreatment with hydrogen peroxide.

15 The process of the invention is preferably carried out using compounds of the formula I where  $z$  is 2 or 3 especially 3 and also compounds in which  $R^1$  is hydrogen or alkyl  $R^1$  has not more than 10 especially not more than 4 carbon atoms.

20 Preference is also given to compounds of formula I where  $R^2$  and  $R^3$  are independently hydrogen, methyl or ethyl and together have not more than 3 preferably only 2 carbon atoms. Preferred metals M are alkali and alkaline earth metals and zinc. Particular preference is given to compounds of this type in which a combination of the abovementioned preferred features is  
25 present, for example a compound of the formula I where  $R^1$ ,  $R^2$  and  $R^3$  are each hydrogen.

30 The compounds of the formula I can also be used as individuals. But it is more advantageous to use mixtures of these compounds in which the  $z$  indices have different meanings, especially mixtures in which the various compounds are present in that ratio which corresponds to their equilibrium concentration in an aqueous system of compounds of the formula I, the amine  
35 or the hydroxylamine of the formula  $R^1_{3-z}NH_z$  and a hydroxyalkanesulfinate of the formula  $HO-CR^2R^3-SO_2M$ , where  $R^1$ ,  $R^2$ ,  $R^3$ ,  $z$  and M are each as defined above and

the molar ratio of sulfur-containing compounds to nitrogen-containing compounds is in the range from 0.2 to 1.1, preferably from 0.25 to 1.0, especially from 0.3 to 0.5.

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It will be appreciated that the process of the invention can also be carried out using mixtures of compounds of the formula I which differ with regard to the meanings of  $R^1$  and/or  $R^2$  and/or  $R^3$ .

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The aminoalkanesulfinates of the formula I can also be used with advantage in mixture with the corresponding aminoalkanesulfonates, in which case these are present in an aminoalkanesulfinic acid:aminoalkanesulfonic acid ratio of from 3:1 to 1:3, preferably from 1.5:1 to 1:1.5 especially in a ratio of about 1:1.

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In a further advantageous embodiment, the textile material is additionally and advantageously concurrently treated with backstain inhibitors and/or dispersants and/or surfactants. These are used in total in an amount of from 0.5 to 10.0 g/l, preferably from 1 to 5 g/l. Backstain inhibitors are effective in particular in preventing the differently colored - or in the case of denim the undyed - weft being (back)stained by the dissolved dye. Examples of backstain inhibitors are polyvinylpyrrolidone, naphthalenesulfonic acid-formaldehyde condensates, oleic acid alkoxylates and fatty acid alkoxylates.

The process of the invention is advantageously carried out at elevated temperature, preferably at 40 - 100°C, especially at 60 - 95°C, specifically at 75 - 90°C, under neutral or weakly acidic conditions, preferably at a pH of from 4 to 7 especially from 5 to 7 and a liquor ratio of from 5:1 to 50:1 preferably from 10:1 to 20:1. The pH may be set using known acids, such as

citric acid, acetic acid or phosphoric acid. The pH may be stabilized by adding a buffer system eg. phosphoric acid/alkali metal phosphate or citric acid/alkali metal citrate, typically in an amount of about 2 g/l. The  
5 compounds of the formula I are used in a concentration of from 0.001 to 0.3 mol/l, preferably from 0.01 to 0.1 mol/l, based on sulfinat.

Under the processing conditions described, the  
10 bleaching time is generally in the range from 5 to 30 minutes, preferably in the range from 10 to 20 minutes, depending on the desired degree of lightening.

15 The stripping effect of the compounds of the formula I is simple to control. The degree of lightening increases with increasing temperature, with increasing bleaching agent concentration and with decreasing pH. Under strong bleaching conditions, the process of the  
20 invention makes it possible to cut the stonewashing time appreciably.

Prior to the process of the invention being carried out, the material which is to be bleached is  
25 advantageously desized. A customary enzymatic desizing process may be employed for this purpose, for example. Furthermore, the textile material may be subjected to a stonewashing process prior to bleaching. Stonewashing is customarily carried out using pumice and/or  
30 cellulases. However, the bleach may also be carried out together with the stonewashing.

If desired, the textile material bleached according to the invention may additionally be subjected to an  
35 oxidative aftertreatment. To this end, the bleached textile material may be treated for example at from 80 to 95°C and a liquor ratio of from 5:1 to 20:1 (eg.



10:1) with from 2 to 8 g/l (eg. 4 g/l) of 38°Bé sodium hydroxide, from 2 to 5 g/l of 50% by weight hydrogen peroxide and from 0.5 to 5 g/l (eg. 1 g/l) of backstain inhibitor, dispersant and/or surfactant for from 5 to 5 15 minutes (eg. 10 minutes).

In a further aftertreatment step, the textile material may be aftertreated as usual with softeners.

- 10 By way of further simplification of the application process, the solutions of the sulfinates or the solutions of the above-described equilibrium mixtures and/or their mixtures with the corresponding aminoalkanesulfonic acids may also be admixed with
- 15 process-specific assistants, for example the abovementioned backstain inhibitors, dispersants and/or surfactants. These preparations likewise form part of the subject-matter of the present invention.
- 20 The aminoalkanesulfinates of the formula I to be used for the bleaching process of the invention, the above-described equilibrium mixtures and the combination of these chemical entities with the corresponding aminoalkanesulfonates are also useful for preparing
- 25 discharge prints on dyeings of vat and sulfur dyes. For discharge printing, the neutral or weakly acidic solutions of the sulfinates or the solutions of the above-described equilibrium mixtures and/or their mixtures with the corresponding aminoalkanesulfonic
- 30 acids are admixed with known thickeners and the thusly obtained discharge print pastes are printed in the desired design on the dyeing to be discharged, subjected to a heat treatment and finished as usual. The process is particularly useful when discharge
- 35 printing is to be carried out in the neutral or weakly acidic pH range and/or when the desired discharge is not to white but half-tone patterns are to be produced.

Useful thickeners for preparing the discharge print pastes include all natural and synthetic substances known for preparing such print pastes, for example carob bean flour, salts of polyacrylic acid or solvent-based thickeners.

The aminoalkanesulfinic acid is prepared according to generally known processes (cf. EP-A-914516), for example by reacting sodium dithionite with 2 mol of an aldehyde or ketone of the general formula  $R^2COR^3$ , where  $R^2$  and  $R^3$  are each as defined above, to obtain a mixture of hydroxyalkane-sulfinic acid and -sulfonate, from which the sulfinic acid may if desired be isolated for further reaction. The sulfinic acid obtained, but preferably the reaction mixture obtained from the reaction of the aldehyde or ketone with alkali metal dithionite, is condensed with ammonia, an amine or a hydroxylamine of the formula  $R^1_{3-z}NH_z$ , where  $R^1$  and  $z$  are each as defined above, in a molar ratio of from 0.2 to 1.1, preferably from 0.25 to 1.0, especially from 0.3 to 0.5, in a suitable solvent, preferably in an aqueous medium, if desired at slightly elevated temperature. This produces a solution of the aminoalkanesulfinic acid or - if the hydroxyalkanesulfinic acid was not first isolated - of a mixture of aminoalkanesulfinic acid and aminoalkane-sulfonate, from which the aminoalkanesulfonate can be removed (cf. K. Reinking, E. Dehnelt, H. Labhardt in Ber. 38, (1905), p. 1069-1080). Advantageously, however, the aminoalkanesulfinates are not isolated from the aqueous solution, nor the sulfonate separated off, and instead the as-obtained reaction mixture is used directly for the process of the invention. These solutions have very good stability in storage and the advantage for the user that the complicated dissolving of a solid substance in water is eliminated and instead the aqueous solution need only be diluted to use

concentration. In addition, automatic process control is made possible as a result.

The process of the invention is useful for the partial  
5 bleaching (lightening) of dyeings and prints with vat  
and sulfur dyes. Dyes whose dyeings or prints are  
bleachable according to the invention are listed in the  
Colour Index under vat dyes and sulfur dyes. Examples  
10 of what is bleachable by the process of the invention  
are dyeings with indigoid dyes, for example indigo,  
dibromoindigo, indigocarmine, tetrabromoindigo,  
tetrachloroindigo or thioindigo; with anthraquinonoid  
dyes, for example Indanthren Blue BC, Indanthren Brown  
NG, Indanthren Brilliant Green FFB, Indanthren  
15 Brilliant Orange GK, Indanthren Brilliant Orange GR,  
Indanthren Brilliant Orange RK, Indanthren Brilliant  
Rose R, Indanthren Brilliant Violet R extra, Indanthren  
Dark Blue BOA, Indanthren Golden Orange G, Indanthren  
Gray M, Indanthren Olive Green B, Indanthren Red RK,  
20 Indanthren Red FBB or Indanthren Reddish Violet RH; or  
with sulfur dyes, for example Immedial Pure Blue, with  
the Hydronblau products particularly important for blue  
workwear, Indocarbon CL and Sulfur Black T.

25 The treatment according to the process of the invention  
is particularly useful for dyeings with indigoid dyes,  
especially with indigo.

Compared with conventional processes, the bleaching  
30 process of the invention has a number of significant  
advantages.

The bleaching agents of the formula I have a reductive  
action and are therefore very gentle on the fiber. By  
35 working in a neutral to weakly acidic medium there is  
no need for the otherwise required costly and  
ecologically unfavorable neutralization.

The aminoalkanesulfinic acids of the formula I and their salts alone or in the embodiments more particularly described above are very useful for the process of the invention, especially because their reactivity is between that of the weak reducing agents, such as glucose or hydroxyacetone, and that of the strong reducing agents, such as hydrosulfite (sodium dithionite) or thiourea dioxide. As a consequence, the dyed textile material is generally decolorized to about 80 - 90%, especially under the conditions of the present invention, if desired nonuniformly.

The backstaining of dissolved dye, for example indigo, on the fibers especially on any differently colored - or in the case of denim material undyed - weft is minimal in that such a weft is left substantially unstained and, if appropriate, a very good contrast is obtained between warp dyeing and weft. The process of the invention is hence a particularly efficient, simple and economical way of achieving the washdown effect. This makes the process of the invention especially useful in jeans washing.

Another surprise is that the portion of the vat or sulfur dye, especially the portion of indigo, which has become redeposited on the fiber is easily removable (for example, by an oxidative aftertreatment with hydrogen peroxide) when the bleach is carried out according to the invention. This removal of indigo deposited on the fiber takes place even though hydrogen peroxide alone is not capable of lightening indigo dyeings.

The oxidative aftertreatment with hydrogen peroxide is thus a preferred embodiment of the present invention, which is preferably employed when backstaining is to be

minimal, when a concentrated liquor is to be used or when a very high degree of lightening is to be achieved in a single wash.

5 The invention further provides for the use of aminoalkanesulfinates of the formula I or of the above-described mixtures thereof for, preferably partial, decolorization (lightening) of vat- or sulfur-dyed textile materials.

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The present invention further provides for the use of aminoalkanesulfinates of the formula I or of the above-described mixtures thereof for preparing discharge prints especially in the half-tone area.

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The example which follows illustrates the invention.

#### **Example**

20 A drum washer is charged with 5 kg of desized and stonewashed jean pants, 100 l of water, 2 g/l of an oleic acid ethoxylate and 1.5 g/l of glacial acetic acid, started, heated to 85°C and at 85°C with 15 ml of a 50% by weight solution containing equimolar amounts  
25 of hydroxymethanesulfinatate condensed with 0.33 mol% of ammonia and hydroxymethanesulfonate condensed with 0.33 mol% of ammonia. The pH is 6.2 and in the course of the bleaching process it rises to 6.5 over 15 minutes. Thereafter the bleaching liquor is dropped hot from the  
30 rotating drum and the textile material is rinsed once with cold water. Some specimens of the pants thus treated are dried, while the others are treated in a liquor ratio of 10:1 with a liquor containing 5 g/l of 50% by weight hydrogen peroxide, 1 g/l of oleic acid  
35 ethoxylate and 4 ml of 38°Bé sodium hydroxide solution at 90°C for 10 minutes. This is followed by a single rinse with water containing 0.5 g/l of citric acid and

3 g/l of a commercially available soft hand agent, and drying.

5 All the jean pants treated in the manner described  
exhibit a conspicuous used look and very good contrast  
between weft and warp threads. There is no sign  
whatsoever of damage to the fabric. The inside pockets  
of the pants not given the oxidative aftertreatment are  
slightly blue, while the inside pockets of the pants  
10 aftertreated with hydrogen peroxide are perfectly  
white.